JS17 Rec'd PCT/PTO 20 APR 2001

FORM PTO-1390 (REV. 5-93) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER 10191/1784
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371	U.S. APPLICATION NO. (If known, see 37 CFR 1.5) 09/830068

INTERNATIONAL APPLICATION NO. PCT/DE99/03198	INTERNATIONAL FILING DATE (05.10.99) 5 October 1999	PRIORITY DATE(S) CLAIMED (21.10 98) 21 October 1998

TITLE OF INVENTION
METHOD AND DEVICE FOR PRODUCING SHAPED CERAMIC BODIES USING SETTER PLATES

APPLICANT(S) FOR DO/EO/US

EISELE, Ulrich

Applicant(s) herewith submit to the United States Designated/Elected Office (DO/EO/US) the following items and other information

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) immediately rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☒ has been transmitted by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ have been transmitted by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)) (unsigned).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
    ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. ☒ A substitute specification and a marked up version thereof.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information: International Search Report, International Preliminary Examination Report and Form PCT/RO/101.

Express Mail No. EL302703932

JC18 Rec'd PCT/PTO 2 0 APR 2001

U.S. APPLICATION NO if known, see 37 C.F.R 1.5 09/830068	INTERNATIONAL APPLICATION NO PCT/DE99/03198	ATTORNEY'S DOCKET NUMBER 10191/1784

17. ☒ The following fees are submitted:

Basic National Fee (37 CFR 1.492(a)(1)-(5)):
Search Report has been prepared by the EPO or JPO $860.00

International preliminary examination fee paid to USPTO (37 CFR 1.482) . . . $690.00

No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) $710 00

Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO $1000.00

International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) $100.00

				CALCULATIONS	PTO USE ONLY
ENTER APPROPRIATE BASIC FEE AMOUNT =				$ 860	
Surcharge of $130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				$	
Claims	Number Filed	Number Extra	Rate		
Total Claims	19 - 20 =	0	X $18.00	$ 0	
Independent Claims	2 - 3 =	0	X $80.00	$ 0	
Multiple dependent claim(s) (if applicable)			+ $270.00	$ 0	
TOTAL OF ABOVE CALCULATIONS =				$860	
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				$	
SUBTOTAL =				$860	
Processing fee of $130.00 for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(f)). +				$	
TOTAL NATIONAL FEE =				$860	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). $40.00 per property +				$	
TOTAL FEES ENCLOSED =				$860	
				Amount to be: refunded	$
				charged	$

a. ☐ A check in the amount of $________________ to cover the above fees is enclosed.

b. ☒ Please charge my Deposit Account No. 11-0600 in the amount of $860.00 to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 11-0600. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

By [signature] RJM 35,952

[signature]
SIGNATURE

Kenyon & Kenyon
One Broadway
New York, New York 10004

Richard L. Mayer, Reg. No. 22,490
NAME

4/20/01
DATE

CUSTOMER NO. 26646

362917

26646
PATENT TRADEMARK OFFICE

09/830068
JC18 Rec'd PCT/PTO 2 0 APR 2001

[10191/1784]

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s)	:	Ulrich EISELE
Serial No.	:	To Be Assigned
Filed	:	Herewith
For	:	METHOD AND DEVICE FOR PRODUCING SHAPED CERAMIC BODIES USING SETTER PLATES
Art Unit	:	To Be Assigned
Examiner	:	To Be Assigned

Assistant Commissioner
for Patents
Washington, D.C. 20231

PRELIMINARY AMENDMENT AND 37 C.F.R. § 1.125 SUBSTITUTE SPECIFICATION STATEMENT

SIR:

Please amend without prejudice the above-identified application before examination, as set forth below.

IN THE SPECIFICATION AND ABSTRACT:

In accordance with 37 C.F.R. § 1.121(b)(3), a Substitute Specification (including the Abstract, but without claims) accompanies this response. It is respectfully requested that the Substitute Specification (including Abstract) be entered to replace the Specification of record.

IN THE CLAIMS:

Without prejudice, please cancel original claims 1 to 18 and add new claims 19 to 37 as follows:

--19. (New) A method for producing a formed body, the formed body including at least one of a formed ceramic body, a ceramic sheet and a multilayer hybrid, the formed body having at least one

EL302 703 932

of a printed circuit trace, a switching element and a plated throughhole, the method comprising the steps of:

disposing a plurality of green bodies containing an organic auxiliary agent between porous setter plates, through which a gaseous, organic, bake-out product escapes from the plurality of green bodies developed during at least one of a sintering operation and a binder removal operation, the step of disposing being performed during at least one of the sintering operation and the binder removal operation; and

introducing a catalytically active substance into at least one of (i) pores of at least one of the porous setter plates and (ii) pores of at least one porous separating layer of the porous setter plates, the catalytically active substance converting the gaseous, organic, bake-out product.

20. (New) The method of claim 19, wherein the catalytically active substance is introduced into the pores of the at least one porous separating layer in the step of introducing.

21. (New) The method of claim 20, wherein the catalytically active substance is introduced into the pores of at least one of the porous setter plates.

22. (New) The method of claim 19, wherein the catalytically active substance is at least one of introduced: (i) into a surface area of at least one of the porous setter plates; (ii) uniformly inside at least one of the porous setter plates; and (iii) the at least one porous separating layer.

23. (New) The method of claim 19, wherein the catalytically active substance oxidizes an organic hydrocarbon compound.

24. (New) The method of claim 19, wherein the catalytically active substance converts a high-molecular, organic hydrocarbon compound to a low-molecular, organic hydrocarbon compound.

25. (New) The method of claim 19, wherein the catalytically active substance includes at least one of platinum, palladium and rhodium.

26. (New) The method of claim 19, wherein the catalytically active substance is in a form of colloids, the colloids having sizes of 3 nm to 100 nm.

27. (New) The method of claim 19, further comprising the step of thermally treating at least one of (i) at least one of the porous setter plates and (ii) the at least one porous separating layer, after the step of introducing the catalytically active substance;

wherein the step of introducing the catalytically active substance is performed by at least one of steeping in a solution and spraying with the solution, the solution containing the catalytically active substance.

28. (New) The method of claim 27, wherein the solution is a metallic-salt solution.

29. (New) The method of claim 28, wherein the metallic-salt solution is an aqueous solution including at least one of $PtCl_6$, $PdCl_2$, $RhCl_3$, platinum acetate, palladium acetate and rhodium acetate.

30. (New) The method of claim 27, wherein the solution includes the catalytically active substance in a concentration of 0.1 g/l to 30 g/l.

31. (New) The method of claim 27, wherein the step of thermally treating is performed in a gas atmosphere that at least one of (i) does not oxidize the catalytically active substance and (ii) reduces the catalytically active substance.

32. (New) The method of claim 27, wherein the step of thermally treating is performed over a time period of 30 minutes to 5 hours at a temperature of 100 degrees Celsius to 700 degrees Celsius.

33. (New) A device for producing a formed body, the formed body including at least one of a formed ceramic body, a ceramic sheet and a multilayer hybrid, the formed body having at least one of a printed circuit trace, a switching element and a plated throughhole, the device comprising:

porous setter plates, a plurality of green bodies containing an organic auxiliary agent being disposable between the porous setter plates, through which a gaseous, organic, bake-

out product escapes from the plurality of green bodies developed during at least one of a sintering operation and a binder removal operation;

wherein:

a catalytically active substance is introduced into at least one of (i) pores of at least one of the porous setter plates and (ii) pores of at least one porous separating layer of the porous setter plates, the catalytically active substance converting the gaseous, organic, bake-out product; and

the porous setter plates include gas outlets.

34. (New) The device of claim 33, wherein the catalytically active substance is introduced to a porous arrangement, the porous arrangement including one of (i) at least two of the porous setter plates and (ii) at least two of the porous separating layers, the porous arrangement being for compressing the plurality of green bodies during the at least one of the sintering operation and the binder removal operation.

35. (New) The device of claim 34, wherein the porous arrangement is permeable for at least one of a low-molecular, gaseous, oxidation product CO, CO_2, H_2O, CH_4 and a hydrocarbon.

36. (New) The method of claim 19, wherein the formed body is a ceramic multilayer hybrid, and the plurality of green bodies includes a stack of a plurality of green sheets arranged in a justified manner one upon the other and provided with at least one of the printed circuit trace, the switching element and the plated-through hole.

37. (New) The method of claim 19, wherein the catalytically active substance is introduced into the pores of the at least one of the porous setter plates in the step of introducing.--.

REMARKS

This Preliminary Amendment cancels without prejudice original claims 1 to 18 in the underlying PCT Application No. PCT/DE99/03198, and adds without prejudice new claims 19 to 37. The new claims conform the claims to U.S. Patent and Trademark Office rules and do not add new matter to the application.

In accordance with 37 C.F.R. § 1.121(b)(3), the Substitute Specification (including the Abstract, but without the claims) contains no new matter. The amendments reflected in the Substitute Specification (including Abstract) are to conform the Specification and Abstract to U.S. Patent and Trademark Office rules or to correct informalities. As required by 37 C.F.R. § 1.121(b)(3)(iii) and § 1.125(b)(2), a Marked Up Version Of The Substitute Specification comparing the Specification of record and the Substitute Specification also accompanies this Preliminary Amendment. In the Marked Up Version, shading indicates added text and bracketing indicates deleted text. Approval and entry of the Substitute Specification (including Abstract) is respectfully requested.

The underlying PCT Application No. PCT/DE99/03198 includes an International Search Report, dated March 9, 2000. The Search Report includes a list of documents that were uncovered in the underlying PCT Application. A copy of the Search Report accompanies this Preliminary Amendment.

The underlying PCT application also includes an International Preliminary Examination Report, dated February 16, 2001. An English translation of the International Preliminary Examination Report accompanies this Preliminary Amendment.

Applicants assert that the subject matter of the present application is new, non-obvious, and useful. Prompt consideration and allowance of the application are respectfully requested.

Respectfully Submitted,

KENYON & KENYON

Dated: 4/20/01

By:
Richard L. Mayer
(Reg. No. 22,490)

One Broadway
New York, NY 10004
(212) 425-7200

366452

11PRTS
09/830068
JC18 Rec'd PCT/PTO 20 APR 2001
[10191/1784]

METHOD AND DEVICE FOR PRODUCING SHAPED CERAMIC BODIES USING SETTER PLATES

Background Information

The present invention is based on a method and a corresponding device for producing shaped ceramic bodies according to the species defined in the generic claims.

Such a method is described, for example, in the German Patent 43 09 005 A1 in which a method was introduced for producing multilayer hybrids from a plurality of ceramic green sheets which contain organic auxiliary agents as binders and sintering aids, and which are provided with printed circuit traces and plated-through holes. The stack of green sheets is pressed together by two porous, ceramic setter plates during sintering and removal of the binder, to ensure the least possible shrinkage and buckling within the green sheets. To achieve a simple separation between the setter plates and the multilayer hybrid after the sintering process, the setter plates were furthermore provided with a porous separating layer made, for example, of aluminum oxide which can be applied by slip casting or silk-screen printing. The organic auxiliary agents in the form of the binder or sintering additive are largely pyrolyzed during the binder removal or sintering, for example, in a hot press under axial pressure, and escape as organic bake-out products. In this context, the escape takes place, inter alia, via the porous setter plates or the applied porous separating layers which are gas-permeable. Damage to the ceramic sheets due to burning out

the organic auxiliary agents too quickly, the diffusion of the broken-up, split-off or partially-burned organic bake-out products through the setter plates, and the maximum portion of hydrocarbons in the oven atmosphere in order to remain below the explosion limiting values are determinant of the speed for the duration of the binder removal and sintering process.

The object of the present invention is to further develop the existing method in such a way that the necessary period of time for the sintering and removal of binder from the shaped ceramic bodies is markedly shortened without, for example, exceeding the explosion limiting values in the oven atmosphere.

Advantages of the Invention

Compared to the related art, the method of the present invention, having the characterizing features of the generic claims, has the advantage that, by introducing a catalytically active substance into the pores of the porous setter plates and/or into the pores of the porous separating layers, a catalytic conversion of the gaseous bake-out products, escaping when baking out the green bodies, is at least partially achieved. The bake-out products are, in particular, decomposition products of the organic auxiliary agents and contain hydrocarbons, among other things.

The escaping bake-out products are preferably converted into less combustible or incombustible gases, so that the method of the present invention makes it possible to bake out more organic auxiliary agents per unit of time than previously, without, for example, the explosion limiting values for hydrocarbons being reached in the oven atmosphere. This

results in a considerable time savings during the sintering and/or removal of the binder from the green bodies, and thus to a shortening of the oven cycles, which means a marked cost reduction and a substantially lower need for investment in oven installations.

Moreover, catalytically converted, low-molecular oxidation or bake-out products diffuse more quickly through the porous setter plates and the optionally provided separating layers, than unconverted, high-molecular bake-out products, which means a further time savings during production. Incidentally, installations, existing owing to the method of the present invention, for the catalytic afterburning of the waste gases carried away from the ceramic green bodies via the setter plates can be designed to be smaller.

In addition to being introduced into the porous setter plates, the catalytically active substance can also be introduced into the porous separating layers, which brings with it advantages from the standpoint of process engineering. In addition, given an appropriate activity of the introduced, catalytically active substance, in some cases it is even sufficient if the substance is only in the porous separating layers, which leads to a markedly reduced need for these sometimes expensive materials. In the same way, for some purposes it can be sufficient if the catalytically active substance is merely introduced into the surface area of the porous setter plates or separating layers, for example, by spraying on or impregnating. This also reduces material costs.

More advantages and advantageous further developments of the present invention are apparent from the measures indicated in the subclaims.

Thus, one particularly advantageous refinement of the method according to the present invention uses starting materials which, at the latest in the course of a thermal aftertreatment of the setter plates and the separating layers, respectively, are converted to form metallic, nano-scale particles and are located in the pores of the setter plates and/or the separating layers.

Also very advantageous is the selection of a metallic-salt solution as starting material for introducing the catalytically active substance, in the case of which no unwanted, in particular inorganic residues remain in the setter plates or separating layers after the thermal aftertreatment.

For faster removal of gaseous bake-out and conversion products, the setter plates can advantageously be provided with additional gas outlets arranged, in particular, parallel to the surface of the setter plates.

Drawing

The single Figure shows a diagrammatic sketch of a ceramic multilayer hybrid composed of a stack of ceramic sheets between two porous setter plates which are separated from the stack of sheets by porous separating layers.

Exemplary Embodiments

Exemplary embodiments of the present invention are explained more precisely in the following with reference to the Figure. A shaped ceramic body, which, for example, can be one ceramic sheet, a stack of ceramic sheets or a ceramic multilayer

hybrid 10 composed of ceramic sheets 1, 2, 3, 4, 5, that is provided with printed circuit traces, switching elements and plated-through holes (not shown in the Figure), is situated between two porous setter plates 20, 21 which, on the surface on the side facing multilayer hybrid 10, are provided with porous separating layers 30, 31. Setter plates 20, 21 are provided with gas outlets 22, e.g. in the form of channels running parallel to the surface of the plates, for more rapid removal of escaping gases. The shaped ceramic body, that is to say, multilayer hybrid 10, exists initially as a green body and, in addition to ceramic components, also contains organic auxiliary agents, e.g. in the form of binders, sintering additives, softeners and residues of solvents.

Setter plates 20, 21 are made of porous, ceramic materials and are gas-permeable for organic bake-out products which develop during binder removal and/or sintering of the shaped ceramic bodies. They are preferably gas-permeable for low-molecular, gaseous oxidation products such as CO, CO_2, H_2O, CH_4, as well as simple hydrocarbons.

The process of sintering and/or removing binder from multilayer hybrid 10 is carried out in a hot press under axial pressure, setter plates 20, 21 in particular preventing sintering shrinkage of multilayer hybrid 10 from occurring in the plane of setter plates 20, 21. Since, because of their fragility, it is very difficult to handle multilayer hybrids 10 from which the binder has been removed, the entire binder removal and sintering process must be carried out in the hot press, although typically less than one hour of 11.5 hr. of firing time is necessary for the actual sintering under pressure. Essentially the removal of binder from multilayer hybrid 10 by gradual bake-out is carried out during the

remaining time, as a result of which the organic auxiliary agents are thermally decomposed to a great extent, or volatize, undecomposed, from the green body and are carried away to the outside through the gas-permeable setter plates. Thus, essentially the time for the diffusion of the cracked or partially-burned, organic constituents through setter plates 20, 21 is speed-determinate for the binder removal process. Since the organic constituents contain a high portion of hydrocarbon compounds, for reasons of operational safety (protection against explosion), the binder removal process must be carried out in such a way that the concentration of hydrocarbons in the oven atmosphere always remains below the explosion limiting values.

Porous separating layers 30, 31 simplify the removal of ready-sintered multilayer hybrid 10 from setter plates 20, 21. For example, the separating layers contain essentially ceramic constituents such as aluminum oxide and are preferably applied on setter plates 20, 21 by silk-screen printing or slip casting. However, the method of the present invention can also be implemented without separating layers 30, 31. Porous separating layers 30, 31, like setter plates 20, 21, are gas-permeable for organic bake-out products from the ceramic green body.

The essence of the present invention is the introduction of a catalytically active substance into setter plates 20, 21 and/or separating layers 30, 31 prior to beginning the actual process of sintering and/or removal of binder from the shaped ceramic bodies, in order to accelerate the implementation of this binder removal process.

Catalytically active noble metals such as palladium, rhodium

or platinum are suitable for this purpose. The specific selection of the catalytically active substance in the individual case is made according to the type of the organic auxiliary agents and their quantity, as well as the sintering or binder-removal temperatures utilized, it always being necessary to take into account the catalytic activity of the respective material and its costs. The catalytically active substance is used specifically to catalytically convert organic auxiliary agents escaping from the green body during sintering and/or binder removal. To that end, it is very advantageous if it is located in the pores of the porous materials of setter plates 20, 21 and/or of porous separating layers 30, 31, where it is easily available for the escaping gases and can develop a suitably high activity. The catalytically active substance catalytically converts the organic hydrocarbon compounds contained in the escaping bake-out products by, for example, oxidizing them or converting high-molecular, organic hydrocarbon compounds to form low-molecular hydrocarbon compounds. In particular, it is used for the oxidation of easily combustible hydrocarbons into incombustible or non-explosive compounds which are then removed via the pores in setter plates 20, 21 and/or separating layers 30, 31, as well as via gas outlets 22.

The catalytically active substance can be introduced into setter plates 20, 21 and separating layers 30, 31, respectively, by dipping setter plates 20, 21 into an appropriate metallic-salt solution, or by spraying the surface area of setter plates 20, 21 with this solution. In this context, setter plates 20, 21 can already have been provided with separating layers 30, 31 beforehand, so that the catalytically active substance is also introduced into separating layers 30, 31.

By dipping, the catalytically active substance is distributed essentially uniformly within setter plates 20, 21, and optionally within separating layers 30, 31, as well. By spraying in particular the side of the porous plates facing the ceramic green body, the catalytically active substance is present largely on the surface on setter plates 20, 21 and separating layers 30, 31, respectively. One skilled in the art must check in the individual case, on the basis of a few simple experiments, which method is the most suitable in each case. Spraying has the advantage that the quantity of catalytically active material used up is relatively small, which means lower material costs. On the other hand, because of the distribution on the surface, only a small part of the volume of setter plates 20, 21 is catalytically active, which means a correspondingly longer or more incomplete catalytic conversion of the organic bake-out products. However, since the catalytically active materials that are possible also differ with respect to their catalytic activity, one skilled in the art, through preliminary experiments, must find in the individual case an optimum between the material costs and the local distribution of the catalytically active substance, as well as the degree of the catalytic conversion and the time resulting for the binder removal.

In further exemplary embodiments, the catalytically active substance is introduced only into separating layers 30, 31, for example, by subsequent spraying, it again being necessary in the individual case to weigh advantages and disadvantages from the standpoint of process engineering against material costs and the time savings attained during the binder removal.

To ensure a homogenous and very fine distribution of the catalytically active substance in setter plates 20, 21 and

separating layers 30, 31, respectively, or in the corresponding surfaces, they are preferably steeped in an aqueous metallic-salt solution containing at least one of the metallic salts $PtCl_6$, $PdCl_2$, $RhCl_3$, platinum acetate, rhodium acetate or palladium acetate. The concentration of the catalytically active substance in this metallic-salt solution is preferably between 0.1 g/l to 30 g/l. Concentrations of 1 g/l to 15 g/l have turned out to be particularly advantageous. In this case, in a setter plate 20 weighing 1 kg, when using a platinum solution containing 10 g of platinum to 1 liter of solution, approximately 0.6 g of platinum is introduced into setter plate 20. When using a solution containing 6 g of palladium to 1 liter of solution, approximately 0.4 g of palladium is introduced per plate.

After setter plates 20, 21 have been sprayed or dipped, a thermal aftertreatment of setter plates 20, 21 with the introduced catalytically active substance is expediently carried out. Depending on the size of the plates, the type of metal introduced and the metallic-salt solution employed, this aftertreatment lasts from 30 minutes to 5 hours at a temperature of 100° C to 700° C. It is preferably carried out in a gas atmosphere, such as air or nitrogen, which does not oxidize the catalytically active substance. However, when working with a few catalytically active materials which can be oxidized relatively easily, in order to avoid oxidation, it is best if work is carried out in a reductive gas atmosphere. For example, in the case of platinum, rhodium and palladium, it is sufficient if the thermal aftertreatment is carried out at 500° C over 2 hr. in air.

The use of organic metallic compounds, such as the acetates indicated, is particularly recommendable for applications in

which no residues of the introduced metallic-salt solution are to remain in setter plates 20, 21 and separating layers 30, 31 after the thermal aftertreatment, since these compounds thermally decompose in a substantially residue-free manner during the thermal aftertreatment.

It has turned out to be particularly advantageous if the catalytically active substance is present in the form of uniformly distributed, nano-scale, metallic colloids of, for example, platinum, rhodium or palladium in the pores of the porous setter plates and separating layers, respectively. The size of these colloids is advantageously between 3 nm and 100 nm, in order to attain the highest possible specific surface areas, and thus an effective seeding of setter plates 20, 21 or of separating layers 30, 31.

What is claimed is:

1. A method for producing formed ceramic bodies, particularly ceramic sheets or multilayer hybrids (10), provided with printed circuit traces, switching elements and/or plated-through holes, which are initially present as green bodies and contain organic auxiliary agents, particularly as binder, the green bodies being disposed during sintering and/or binder removal between porous setter plates (20, 21) through which gaseous, organic, bake-out products of the green bodies escape, the products developing during the sintering and/or binder removal, wherein a catalytically active substance, that catalytically converts the escaping, gaseous, organic, bake-out products from the green bodies, is introduced into the pores of the porous setter plates (20, 21).

2. A method for producing formed ceramic bodies, particularly ceramic sheets or multilayer hybrids (10), provided with printed circuit traces, switching elements and/or plated-through holes, which are initially present as green bodies and contain organic auxiliary agents, particularly as binder, the green bodies being disposed during sintering and/or binder removal between porous setter plates (20, 21) which are provided with porous separating layers (30, 31); gaseous, organic, bake-out products of the green bodies, the products developing during sintering and/or binder removal, escaping through the porous setter plates (20, 21) and the porous separating layers (30, 31), wherein a catalytically active substance, that catalytically converts the escaping, gaseous, organic, bake-out products from the green bodies, is introduced into the pores of the porous separating layers (31, 30).

3. The method as recited in Claim 2, wherein the catalytically active substance is introduced into the pores of the porous setter plates (20, 21), as well.

4. The method as recited in Claim 1, 2 or 3, wherein the catalytically active substance is introduced into the surface area or uniformly inside the porous setter plates (20, 21) and/or the separating layers (30, 31).

5. The method as recited in at least one of the preceding claims, wherein the catalytically active substance oxidizes organic hydrocarbon compounds.

6. The method as recited in at least one of the preceding claims, wherein the catalytically active substance converts high-molecular, organic hydrocarbon compounds to form low-molecular, organic hydrocarbon compounds.

7. The method as recited in at least one of the preceding claims, wherein the catalytically active substance contains at least one of the elements platinum, palladium or rhodium.

8. The method as recited in at least one of the preceding claims, wherein the catalytically active substance is present in the form of colloids having sizes of 3 nm to 100 nm.

9. The method as recited in at least one of the preceding claims, wherein the catalytically active substance is introduced into the porous setter plates (20, 21) and/or the porous separating layers (30, 31) by steeping in a solution or spraying with a solution containing the catalytically active

substance, a thermal aftertreatment of the porous setter plates (20, 21), or of the porous setter plates (20, 21) with the applied porous separating layers (30, 31), being carried out after the introduction of the catalytically active substance.

10. The method as recited in Claim 9, wherein the solution having the catalytically active substance is a metallic-salt solution.

11. The method as recited in Claim 10, wherein the metallic-salt solution is an aqueous solution containing at least one of the metallic salts $PtCl_6$, $PdCl_2$, $RhCl_3$, platinum acetate, palladium acetate or rhodium acetate.

12. The method as recited in at least one of Claims 9 through 11, wherein the solution contains the catalytically active substance in a concentration of 0.1 g/l to 30 g/l.

13. The method as recited in at least one of Claims 9 through 12, wherein the thermal aftertreatment is carried out in a gas atmosphere which does not oxidize the catalytically active substance or which reduces the catalytically active substance.

14. The method as recited in at least one of Claims 9 through 13, wherein the thermal aftertreatment is carried out over a period of time of 30 min. to 5 hr. at a temperature of 100° C to 700° C.

15. A device for carrying out the method as recited in at least one of the preceding claims, wherein the porous setter plates (20, 21) are provided with gas outlets (22).

16. The device for carrying out the method as recited in at least one of Claims 1 through 14 or as recited in Claim 15, characterized by at least two porous setter plates (20, 21), or by at least two porous setter plates (20, 21) that are provided with porous separating layers (30, 31), which compress the green body during sintering and/or binder removal.

17. The device as recited in Claim 15 or 16, wherein the porous setter plates (20, 21), or the porous setter plates (20, 21) with the porous separating layers (30, 31), are permeable for low-molecular, gaseous, oxidation products, particularly for CO, CO_2, H_2O, CH_4, as well as simple hydrocarbons.

18. Use of the method as recited in at least one of Claims 1 through 14 for producing ceramic multilayer hybrids (10) from stacks of a plurality of green sheets (1, 2, 3, 4, 5) that are arranged in a justified manner one upon the other and are provided with printed circuit traces, switching elements and/or plated-through holes.

Abstract

A method and a device for producing shaped ceramic bodies, particularly ceramic sheets or multilayer hybrids (10) provided with printed circuit traces, switching elements and/or plated-through holes. The shaped ceramic bodies are initially present as green bodies and also contain organic auxiliary agents, e.g. as binder. During sintering and/or removal of binder from the shaped ceramic bodies, they are compressed between porous setter plates (20, 21) in whose pores a catalytically active substance is introduced, so that the gaseous, organic, bake-out products of the green bodies, these products developing during sintering and/or binder removal, are catalytically converted when escaping through the porous setter plates. The setter plates can furthermore be provided with separating layers which likewise can contain the catalytically active substance. The proposed method leads to a considerable time savings when sintering and/or removing binder from the shaped ceramic bodies.

Figure

366433

09/830068
JC18 Rec'd PCT/PTO 20 APR 2001

[10191/1784]

METHOD AND DEVICE FOR PRODUCING SHAPED CERAMIC BODIES USING SETTER PLATES

FIELD OF THE INVENTION

The present invention relates to a method and a device for producing shaped ceramic bodies.

BACKGROUND INFORMATION

In German Published Patent Application No. 43 09 005 is discussed a method for producing multilayer hybrids from a plurality of ceramic green sheets which contain organic auxiliary agents as binders and sintering aids, and which are provided with printed circuit traces and plated-through holes. The stack of green sheets is pressed together by two porous, ceramic setter plates during sintering and removal of the binder, to ensure the least possible shrinkage and buckling within the green sheets. To achieve a simple separation between the setter plates and the multilayer hybrid after the sintering process, the setter plates are provided with a porous separating layer made, for example, of aluminum oxide which can be applied by slip casting or silk-screen printing. The organic auxiliary agents in the form of the binder or sintering additive are largely pyrolyzed during the binder removal or sintering, for example, in a hot press under axial pressure, and escape as organic bake-out products. In this context, the escape takes place, in part, via the porous setter plates or the applied porous separating layers which are gas-permeable. Damage to the ceramic sheets may result from burning out the organic auxiliary agents too quickly. Damage may result from the diffusion of the broken-up,

 EL302703932

split-off or partially-burned organic bake-out products through the setter plates. It is believed that there is a maximum portion of hydrocarbons in the oven atmosphere (to remain below the explosion limiting values) determine the speed for the duration of the binder removal and sintering process.

SUMMARY OF THE INVENTION

An object of an exemplary method of the present invention is to provide a method in which the necessary period of time for the sintering and removal of binder from the shaped ceramic bodies is markedly shortened, without, for example, exceeding the explosion limiting values in the oven atmosphere.

It is believed that the exemplary method of the present invention has the advantage that, by introducing a catalytically active substance into the pores of the porous setter plates and/or into the pores of the porous separating layers, a catalytic conversion of the gaseous bake-out products that escape when baking out the green bodies is at least partially achieved. The bake-out products are, in one exemplary embodiment, decomposition products of the organic auxiliary agents and contain hydrocarbons, among other things.

The escaping bake-out products are, in an exemplary embodiment, converted into less combustible or incombustible gases. In this manner, an exemplary method of the present invention may be used to bake out more organic auxiliary agents per unit of time than previously, without, for example, the explosion limiting values for hydrocarbons being reached in the oven atmosphere. It is believed that this results in a considerable time savings during the sintering and/or removal

of the binder from the green bodies, and thus to a shortening of the oven cycles, which should mean a marked cost reduction and a substantially lower need for investment in oven installations.

Moreover, it is believed that catalytically converted, low-molecular oxidation or bake-out products diffuse more quickly through the porous setter plates and the optionally provided separating layers than unconverted, high-molecular bake-out products, which may mean a further time savings during production. According to one exemplary method and/or device of the present invention, installations for the catalytic afterburning of the waste gases carried away from the ceramic green bodies via the setter plates may be smaller.

According to one exemplary embodiment of the present invention, in addition to being introduced into the porous setter plates, the catalytically active substance may also be introduced into the porous separating layers, which is believed to bring with it advantages from the standpoint of process engineering. In an alternative exemplary embodiment, given an appropriate activity of the introduced, catalytically active substance, it may even be sufficient if the substance is only in the porous separating layers, which should lead to a markedly reduced need for these sometimes expensive materials. In the same way, for some purposes it may be sufficient if the catalytically active substance is merely introduced into the surface area of the porous setter plates or separating layers, for example, by spraying on or impregnating. This may also reduce material costs.

Thus, in one exemplary method according to the present

invention, starting materials may be used which, in the course of a thermal after-treatment of the setter plates and/or the separating layers, respectively, are converted to form metallic, nano-scale particles in the pores of the setter plates and/or the separating layers.

Another exemplary embodiment involves the selection of a metallic-salt solution as the starting material for introducing the catalytically active substance. In this exemplary embodiment there may be no unwanted, in particular inorganic, residues remaining in the setter plates and/or separating layers after the thermal after-treatment.

For faster removal of gaseous bake-out and conversion products, it is believed that the setter plates may be provided with additional gas outlets arranged, in particular, parallel to the surface of the setter plates.

BRIEF DESCRIPTION OF THE DRAWING

The Figure shows a ceramic multilayer hybrid composed of a stack of ceramic sheets between two porous setter plates which are separated from the stack of sheets by porous separating layers.

DETAILED DESCRIPTION

A shaped ceramic body, which, for example, can be one ceramic sheet, a stack of ceramic sheets or a ceramic multilayer hybrid 10 composed of ceramic sheets 1, 2, 3, 4, 5, and which is provided with printed circuit traces, switching elements and plated-through holes (not shown in the Figure), is situated between two porous setter plates 20, 21. The two porous setter plates 20, 21 may, on the surface on the side

facing multilayer hybrid 10, be provided with porous separating layers 30, 31. Setter plates 20, 21 may be provided with gas outlets 22, e.g. in the form of channels running parallel to the surface of the plates, for more rapid removal of escaping gases. The shaped ceramic body (that is, multilayer hybrid 10) may exist initially as a green body and, in addition to ceramic components, may also contain organic auxiliary agents, e.g. in the form of binders, sintering additives, softeners and residues of solvents.

Setter plates 20, 21 may be made of porous, ceramic materials and may be gas-permeable for organic bake-out products which develop during binder removal and/or sintering of the shaped ceramic bodies. They may be preferably gas-permeable for low-molecular, gaseous oxidation products such as CO, CO_2, H_2O, CH_4, as well as simple hydrocarbons.

The process of sintering and/or removing binder from multilayer hybrid 10 is carried out in a hot press under axial pressure, setter plates 20, 21 in particular may prevent sintering shrinkage of multilayer hybrid 10 from occurring in the plane of setter plates 20, 21. Since, because of their fragility, it is very difficult to handle multilayer hybrids 10 from which the binder has been removed, the entire binder removal and sintering process must be carried out in the hot press, although "typically" less than one hour of 11.5 hr. of firing time is necessary for the actual sintering under pressure. Essentially, the removal of binder from multilayer hybrid 10 by gradual bake-out is carried out during the remaining time, as a result of which the organic auxiliary agents are thermally decomposed to a great extent, or volatize, undecomposed, from the green body and are carried

away to the outside through the gas-permeable setter plates. Thus, essentially, the time for the diffusion of the cracked or partially-burned, organic constituents through setter plates 20, 21 is speed-determinate for the binder removal process. Since the organic constituents contain a high portion of hydrocarbon compounds, for reasons of operational safety (protection against explosion), the binder removal process must be carried out so that the concentration of hydrocarbons in the oven atmosphere always remains below the explosion limiting values.

Porous separating layers 30, 31 simplify the removal of ready-sintered multilayer hybrid 10 from setter plates 20, 21. For example, the separating layers contain essentially ceramic constituents such as aluminum oxide and are preferably applied on setter plates 20, 21 by silk-screen printing or slip casting. The exemplary method of the present invention, however, can also be implemented without separating layers 30, 31. Porous separating layers 30, 31, like setter plates 20, 21, are gas-permeable for organic bake-out products from the ceramic green body.

One aspect of the exemplary method and/or device of the present invention is the introduction of a catalytically active substance into setter plates 20, 21 and/or separating layers 30, 31 prior to beginning the actual process of sintering and/or removal of binder from the shaped ceramic bodies, in order to accelerate the implementation of this binder removal process.

Catalytically active noble metals such as palladium, rhodium or platinum are believed to be suitable for this purpose. The

specific selection of the catalytically active substance in the individual case is made according to the type of the organic auxiliary agents and their quantity, as well as the sintering or binder-removal temperatures utilized, it always being important and/or necessary to take into account the catalytic activity of the respective material and its costs. The catalytically active substance is used specifically to catalytically convert organic auxiliary agents escaping from the green body during sintering and/or binder removal. To that end, it is believed to be very advantageous if it is located in the pores of the porous materials of setter plates 20, 21 and/or of porous separating layers 30, 31, where it is easily available for the escaping gases and can develop a suitably high activity. The catalytically active substance catalytically converts the organic hydrocarbon compounds contained in the escaping bake-out products by, for example, oxidizing them or converting high-molecular, organic hydrocarbon compounds to form low-molecular hydrocarbon compounds. In particular, it is used for the oxidation of easily combustible hydrocarbons into incombustible or non-explosive compounds which are then removed via the pores in setter plates 20, 21 and/or separating layers 30, 31, as well as via gas outlets 22.

The catalytically active substance can be introduced into setter plates 20, 21 and separating layers 30, 31, respectively, by dipping setter plates 20, 21 into an appropriate metallic-salt solution, or by spraying the surface area of setter plates 20, 21 with this solution. In this context, setter plates 20, 21 can already have been provided with separating layers 30, 31 beforehand, so that the catalytically active substance is also introduced into

separating layers 30, 31.

By dipping, the catalytically active substance is distributed essentially uniformly within setter plates 20, 21, and optionally within separating layers 30, 31, as well. By spraying in particular the side of the porous plates facing the ceramic green body, the catalytically active substance is present largely on the surface on setter plates 20, 21 and separating layers 30, 31, respectively. Spraying has the advantage that the quantity of catalytically active material used up is relatively small, which means lower material costs. On the other hand, because of the distribution on the surface, only a small part of the volume of setter plates 20, 21 is catalytically active, which means a correspondingly longer or less complete catalytic conversion of the organic bake-out products.

In further exemplary embodiments, the catalytically active substance is introduced only into separating layers 30, 31, for example, by subsequent spraying. In this case again, it would be important and/or necessary in the individual case to weigh advantages and disadvantages from the standpoint of process engineering against material costs and the time savings attained during the binder removal.

To ensure a homogenous and very fine distribution of the catalytically active substance in setter plates 20, 21 and separating layers 30, 31, respectively, or in the corresponding surfaces, they are in an exemplary embodiment steeped in an aqueous metallic-salt solution containing at least one of the metallic salts $PtCl_6$, $PdCl_2$, $RhCl_3$, platinum acetate, rhodium acetate or palladium acetate. The

concentration of the catalytically active substance in this metallic-salt solution may be between 0.1 g/l to 30 g/l. Concentrations of 1 g/l to 15 g/l have turned out to be particularly advantageous. In this case, in a setter plate 20 weighing 1 kg, when using a platinum solution containing 10 g of platinum to 1 liter of solution, approximately 0.6 g of platinum is introduced into setter plate 20. When using a solution containing 6 g of palladium to 1 liter of solution, approximately 0.4 g of palladium is introduced per plate.

After setter plates 20, 21 have been sprayed or dipped, a thermal after-treatment of setter plates 20, 21 with the introduced catalytically active substance is expediently carried out. Depending on the size of the plates, the type of metal introduced and the metallic-salt solution employed, this after-treatment lasts from 30 minutes to 5 hours at a temperature of 100° C to 700° C. This may be carried out in a gas atmosphere, such as air or nitrogen, which does not oxidize the catalytically active substance. However, when working with a few catalytically active materials which can be oxidized relatively easily, in order to avoid oxidation, it is believed to be best if work is carried out in a reductive gas atmosphere. For example, in the case of platinum, rhodium and palladium, it is sufficient if the thermal after-treatment is carried out at 500° C over 2 hr. in air.

The use of organic metallic compounds, such as the acetates indicated, is particularly recommendable for applications in which no residues of the introduced metallic-salt solution are to remain in setter plates 20, 21 and separating layers 30, 31 after the thermal after-treatment, since these compounds thermally decompose in a substantially residue-free manner

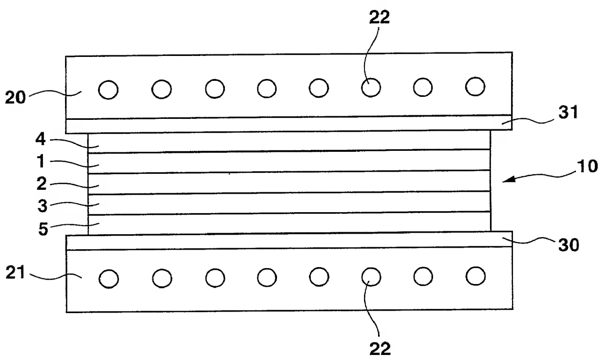
during the thermal after-treatment.

In another exemplary embodiment, the catalytically active substance is present in the form of uniformly distributed, nano-scale, metallic colloids of, for example, platinum, rhodium or palladium in the pores of the porous setter plates and separating layers, respectively. It is believed that the size of these colloids is advantageously between 3 nm and 100 nm, in order to attain the highest possible specific surface areas, and thus an effective seeding of setter plates 20, 21 or of separating layers 30, 31.

ABSTRACT OF THE DISCLOSURE

A method and device for producing shaped ceramic bodies, particularly ceramic sheets or multilayer hybrids provided with printed circuit traces, switching elements and/or plated-through holes. The shaped ceramic bodies are initially present as green bodies and also contain organic auxiliary agents, for example as a binder. During sintering and/or removal of the binder from the shaped ceramic bodies, they are compressed between porous setter plates in whose pores a catalytically active substance is introduced, so that the gaseous, organic, bake-out products of the green bodies, these products developing during sintering and/or binder removal, are catalytically converted when escaping through the porous setter plates. The setter plates be provided with separating layers that likewise may contain the catalytically active substance. The method should provide a considerable time savings when sintering and/or removing binder from the shaped ceramic bodies.

366437


22
20
31
4
1
10
2
3
5
30
21
22

[10191/1784]

DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled **METHOD AND DEVICE FOR PRODUCING SHAPED CERAMIC BODIES USING SETTER PLATES**, the specification of which was filed as International Application No. **PCT/DE99/03198** on October 5, 1999.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, § 1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, § 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application(s) for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

EL244504546

PRIOR FOREIGN APPLICATION(S)

Number	Country filed	Day/month/year	Priority Claimed Under 35 USC 119
198 48 474.7	Fed. Rep. of Germany	21 October 1998	Yes

And I hereby appoint Richard L. Mayer (Reg. No. 22,490) and Gerard A. Messina (Reg. No. 35,952) my attorneys with full power of substitution and revocation, to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.

Please address all communications regarding this application to:

KENYON & KENYON
One Broadway
New York, New York 10004

26646
PATENT TRADEMARK OFFICE

Please direct all telephone calls to Richard L. Mayer at (212) 425-7200.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful and false statements may jeopardize the validity of the application or any patent issued thereon.

100

Inventor: **Ulrich EISELE**

Inventor's Signature: U. Eisele

Date: 30.4.2001

Residence: Boecklerstr. 6B
70199 Stuttgart
Federal Republic of Germany DEX

Citizenship: Federal Republic of Germany

Post Office Address: Same as above.

363148